

Oxidation of Activated Phenols by Dioxygen Catalysed by the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ Heteropolyanion

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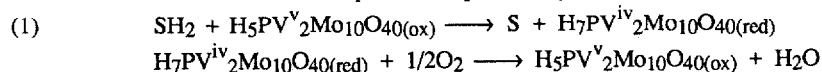
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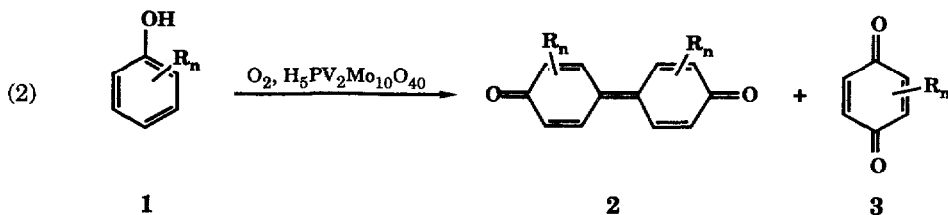
Abstract: The $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ heteropolyanion has been found to catalyse the highly selective aerobic oxidation of dialkylphenols to diphenoquinones and the oxidation of 2, 3, 5-trimethylphenol to the 2, 3, 5-trimethyl-1, 4-benzoquinone. The rate is highly dependent on the oxidation potential of the substrate and is proceeds by electron transfer from the phenol substrate to the heteropolyanion catalyst.

The ecological concerns surrounding the use of toxic and dangerous albeit very effective stoichiometric oxidants such as chromate and permanganate etc. in the synthesis of fine chemicals has spurred an increasing amount of research into new catalytic systems which use clean and inexpensive primary oxidants especially dioxygen and hydrogen peroxide¹. In this context there has been recent interest in the catalytic activity of heteropolyanions generally of the Keggin structure, $\text{XM}'_n\text{M}_{12-n}\text{O}_{40}^{y-}$ ($X = \text{P, Si; M} = \text{Mo, W; M}' = \text{V; } n = 0 - 6$). Thus, hydrogen peroxide has been used as oxidant in two phase catalytic reactions with the $\text{XM}_{12}\text{O}_{40}^{y-}$ heteropolyanions and an non-symmetrical quaternary ammonium cation for the epoxidation of alkenes², allyl alcohols³, and β -unsaturated acids⁴ and the oxidation of alcohols⁵, alkynes⁶, and phenol⁷. Some recent mechanistic studies⁸ have, however, additionally indicated that the original heteropolyanion is in fact only a catalytic precursor to a simpler catalytic peroxide species, $\text{PO}_4[\text{WO}(\text{O}_2)_2]_4^{3-}$ which had been previously identified⁹.

Entirely different reaction modes have been utilized for oxidations with dioxygen as primary oxidant in both photochemical¹⁰ and normal thermal systems. In the later case, $\text{H}_{3+n}\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}$ (usually $n = 2$) has been used as a secondary oxidant in place of CuCl_2 in Wacker type reactions¹¹, in the oxidation of HBr ¹² and sulfides¹³, the oxidative cleavage of ketones¹⁴, and oxidative dehydrogenation of dienes¹⁵, alcohols and amines¹⁶. These later reactions are pictured to proceed by the following generalized reaction scheme, eq 1.



In this manuscript we wish to report on the aerobic dehydrodimerization of dialkylphenols and the oxidation of 2, 3, 5-trimethyl phenol to the vitamin E intermediate 2, 3, 5-trimethyl-1, 4-benzoquinone eq 2,



Results and Discussion

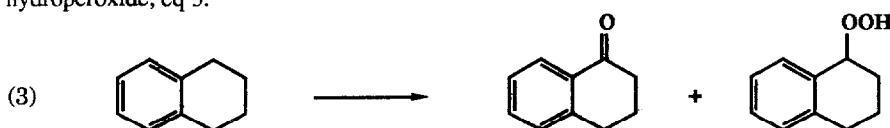
Reactions were carried out in a homogenous reaction phase at 60 °C by dissolving 1 mmol dialkylphenol, **1**, and 0.02 mmol $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ in 20 ml n-hexanol under a oxygen (1 atm) atmosphere. After the reaction's completion the products were quantified either by isolation of the semicarbazone derivative¹⁷ or by HPLC analysis¹⁸. From Table 1 showing both reaction yields and the oxidation potential of the phenol substrate, one can see that the sole product in the oxidation of the dialkylphenols is the dimeric diphenoquinone, **2**. Furthermore, the yield is proportional to the oxidation potential of the phenol substrate. On the other hand, the more reactive 2, 3, 6 trimethylphenol exclusively yielded the monomeric benzoquinone, **3**. In a comparison of the results of the dialkylphenol oxidation with results obtained by two often used catalysts for this reaction, mainly the copper(II)chloride-amine complexes¹⁹ and the cobalt based compounds²⁰ and also recently the manganese substituted heteropolyanion²¹, $\text{SiMnW}_{11}\text{O}_{39}^{5-}$, one observes that the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ heteropolyanion catalyses formation of diphenoquinones whereas generally the cobalt and manganese systems yield benzoquinones as the major product along only minor amounts of diphenoquinones. Copper catalysts^{19,22} also have tended to yield diphenoquinones as the major product, however their activity is strongly dependent on reaction conditions, they are often less reactive and selective and yield a variety of additional side products including chlorinated phenols and polymeric ethers.

Table 1. Aerobic Oxidation of Alkylated Phenols Catalysed by the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ Heteropolyanion.

Substrate	Product	Conversion (yield)	Oxidation Potential, $E^\circ(\text{V})$
2, 6-di-tert-butylphenol	3, 3', 5, 5'-tetra-tert-butyl diphenoquinone	100 (96) ^a	0.68
2, 6-dimethylphenol	3, 3', 5, 5'-tetra-methyl diphenoquinone	80 (80)	0.76
2, 5-dimethylphenol	2, 2', 5, 5'-tetra-methyl diphenoquinone	50 (47) ^b	0.82
3, 5-dimethylphenol	2, 2', 6, 6'-tetra-methyl diphenoquinone	0 (0) ^b	0.86
2, 3, 5-trimethylphenol	2, 3, 5-trimethyl-1,4-benzoquinone	75 (73) ^c	0.69

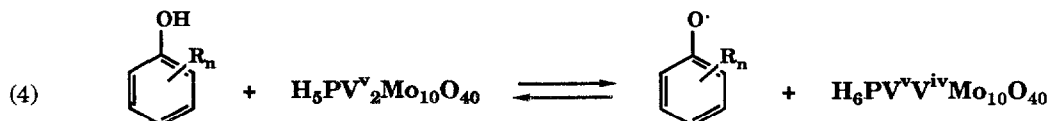
Reaction Conditions: 1 mmol substrate, 0.02 mmol $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, 20 ml n-hexanol, 1 atm dioxygen, 60 °C, 4 hr, conversions were computed by HPLC and yields given by isolated quantities. a) 25 °C b) 90 hr c) similar yields were found with ethanol, n-propanol and n-butanol as solvents.

In addition to the significant synthetic value of such inherently selective reactions we believe that inverse and high selectivity of the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ catalyst relative to the cobalt, manganese and copper systems along with the strong rate dependency on the oxidation potential of the organic substrate yields important insights into the possible mechanism of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ catalysed oxidations. Since it has been shown that the cobalt and manganese compounds catalyse the formation of benzoquinones by metal catalysed autoxidations²³ the different selectivity found for $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ would *a priori* indicate an entirely different mechanism. In order to test this hypothesis tetralin was autoxidised in a non-catalytic reaction to a mixture of α -tetralone and α -tetralin hydroperoxide, eq 3.



Thus, in a reaction performed at 70 °C for 24 hr, with 1 atm dioxygen, tetralin yielded 25.2% hydroperoxide and 10.1% ketone. An identical reaction with 0.2 mol% $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ showed no tetralin turnover indicating complete suppression of autoxidation. The mode by which the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ catalyst inhibits autoxidation is unknown, but a plausible explanation is that thermally formed tetralin or tetralin peroxide radicals react very quickly with the heteropolyanion terminating the propagation of the radical chain reaction.

Another important facet of these phenol oxidations by $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ heteropolyanion concerns the reaction's strong dependence on the oxidation potential of the phenol substrate. Measurement by cyclic voltammetry of the oxidation potential of the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ catalyst in a apolar solvent such as dichloromethane (the catalyst is dissolved in this phase by addition of tetraglyme) shows an oxidation potential of 0.81 V. Therefore, phenols with a oxidation potential less than that of the catalyst will react while those with a greater potential will be inert and one may conclude that the thermodynamics of the interaction between the organic phenol and the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ catalyst, eq 4, will determine whether the reaction proceeds.



This thermodynamic control by the first electron transfer step of the reaction is significant keeping in mind that the reaction with any phenol would be thermodynamically favorable in its entirety due to the large free energy of reaction gained in the conversion of dioxygen to water. The electron transfer can be monitored visibly or by UV-vis spectroscopy whereby reactive compounds interact by with $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ forming reduced heteropolyanion blue compounds. An interaction with a one electron donor as previously found for compounds such as limonene¹⁵ and in this case with phenols gives a green reduced heteropolyanion and a phenoxy radical. It is not clear whether these species are free radicals or whether they are phenol-heteropolyanion intermediates. The fact that phenoxy radicals thus formed may either combine to yield the diphenoquinone as found for the dialkylphenols or insert dioxygen as found for trimethylphenol resulting in the benzoquinone product, suggests that the nature of the phenol - catalyst interaction and phenoxy radical is also a function of the oxidation potential.

One may conclude by stating that the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ heteropolyanion is a highly selective catalyst for the aerobic oxidation of polyalkylphenols with a basic product profile similar to copper catalysed reactions, however with higher reactivities, selectivities and fewer by products. The oxidation potential of the phenol

substrate is decisive in determining whether the reaction will take place and possibly also the nature of the product. At present further research efforts are being made to develop new synthetic applications and to study the mechanistic aspects of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ heteropolyanion catalysed aerobic oxidations.

References and Notes

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- The similarity of CuCl_2 catalysed oxidations with that of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ oxidations was first noted in Wacker type reactions (ref 11) with the significant advantage of the latter being that the chlorinated side products are eliminated.
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